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PATENT ABSTRACTS OF JAPAN

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(54) HIGHLY HEAT-RESISTANT POLYPROPYLENE FIBER

(57)Abstract:

PROBLEM TO BE SOLVED: To provide as a cement-reinforcing material highly heat-resistant polypropylene filaments or yarn which do not melt at an autoclave curing temperature of 175 to 180°C and has an excellent shape retention property.

SOLUTION: The polypropylene filaments or yarn produced by melt-spinning homo polypropylene resin having an isotactic pentad fraction of 96 to 98.5% and a melt flow rate of 0.1 to 30 g/10 min (230°C, 2.16 kg load) and then drawing the filaments, has a heat shrinkage rate of ≤10% at 170°C for 10 min and a melt peak temperature of ≥178°C.

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CLAIMS

[Claim(s)]
[Claim 1] The high thermal-resistance polypropylene fiber or yarn to which it is the polypropylene fiber or yarn which comes to extend the gay polypropylene resin whose melt flow rates (230 degrees C, 2.16kg load) an isotactic pentad fraction is less than 98.5% 96% or more, and are 0.1-30g / 10 minutes after melting fabrication, and 170 degrees C and the rate of a thermal contraction for 10 minutes are characterized by dissolution peak temperature being 178 degrees C or more 10% or less.
[Claim 2] The high thermal-resistance polypropylene fiber according to claim 1 or yarn characterized by heat-treating the polypropylene fiber or yarn after extension at 170-195 degrees C under restricted strain.
[Claim 3] The high thermal-resistance polypropylene fiber according to claim 1 or 2 or yarn characterized by the dissolution peak which measured the polypropylene fiber or yarn before restricted heat treatment in the state of the restraint existing in 180 degrees C or more.
[Claim 4] Fiber for cement reinforcement characterized by the bird clapper from a high thermal-resistance polypropylene fiber or yarn given in any 1 term of claims 1-3.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] Especially this invention relates to the high thermal-resistance polypropylene fiber or yarn used as fiber for cement reinforcement about a high thermal-resistance polypropylene fiber or yarn.
[0002]
[Description of the Prior Art] The cement moldings is used for interior material, a sheathing material, roofing, etc. as a building-materials use from the former. Although the product which added asbestos fiber from the former is widely used as fiber for reinforcement of these cement moldings, the bad influence to asbestine health is regarded as questionable in recent years as especially an environmental problem becomes severe, and use of this alternative fiber is increasing every year. As fiber for reinforcement which substitutes for this asbestos, polyolefine fiber, such as a polypropylene fiber and a polyethylene fiber, is beginning to be especially used as alternative fiber which does not have a bad influence in a human body in recent years.
[0003] In the stage of performing the fabrication, cement needs regimen process. 170-180 degrees C of regimens are performed within an autoclave (10 kgf/cm2) for dozens hours. However, in the usual polypropylene fiber, since the melting point is 160-165 degrees C, bearing this regimen cannot be finished, it dissolves and the problem to which polypropylene does not exist as fiber in cement concrete after a regimen end arises. When lowering the curing temperature of cement concrete to 165-170 degrees C, it was needed for the regimen for a long time, and there were problems, such as causing a productivity fall.
[0004]
[Problem(s) to be Solved by the Invention] From the above-mentioned viewpoint, as cement reinforcing materials, the purpose of this invention does not tend to be dissolved at the autoclave-curing temperature of 175-180 degrees C, but tends to offer a high thermal-resistance polypropylene fiber or yarn excellent in form maintenance nature.
[0005]
[Means for Solving the Problem] As a result of inquiring wholeheartedly that the above-mentioned technical problem should be attained, by heat-treating the gay polypropylene resin which has specific stereoregularity and a fluidity at specific temperature under restricted strain after melting extension, this invention persons found out that the rate of a thermal contraction under an elevated temperature could be stopped low, and dissolution peak temperature could be made high, and completed this invention.
[0006] That is, invention of the 1st of this invention is the polypropylene fiber or yarn which comes to extend the gay polypropylene resin whose melt flow rates (230 degrees C, 2.16kg load) an isotactic pentad fraction is less than 98.5% 96% or more, and are 0.1-30g / 10 minutes after melting fabrication, and 170 degrees C and the rate of a thermal contraction for 10 minutes are the high thermal-resistance polypropylene fibers or yarn to which dissolution peak temperature is characterized by being 178 degrees C or more 10% or less.
[0007] Moreover, invention of the 2nd of this invention is a high thermal-resistance polypropylene fiber or yarn given in the 1st invention characterized by heat-treating the polypropylene fiber or yarn

[0008] Moreover, invention of the 3rd of this invention is a high thermal-resistance polypropylene fiber or yarn given in invention of the 1st or 2 characterized by the dissolution peak which measured the polypropylene fiber or yarn before restricted heat treatment in the state of the restraint existing in 180 degrees C or more.
[0009] Moreover, invention of the 4th of this invention is fiber for cement reinforcement characterized by the bird clapper from a high thermal-resistance polypropylene fiber or yarn given in the 1-3rd ones of invention.
[0010]
[Embodiments of the Invention] Hereafter, this invention is explained in detail.
1. The isotactic pentad fraction (it abbreviates to IPF hereafter.) whose polypropylene resin in a polypropylene resin this invention is the index of stereoregularity is less than 98.5% 96% or more, and the melt flow rates (it abbreviates to MFR hereafter.) in 230 degrees C and 2.16kg load are 0.1-30g / gay polypropylene resin that satisfies 0.5-25g / 10 minutes preferably for 10 minutes. The melting temperature of gay polypropylene itself and its fiber moldings becomes it low that IPF is less than 96%, it is unsuitable as cement reinforcing materials, and on the other hand, at the time of melt spinning, crystallization of a melting resin is remarkable and spinning stability, such as a thread shake, is early spoiled in connection with a bird clapper as IPF is 98.5% or more. Moreover, since the pressure of a dice outlet rises too much that MFRs are 0.1g / less than 10 minutes at the time of melting fabrication (mainly spinning of fiber), if MFR, on the other hand, exceeds 30g / 10 minutes preferably, the amount component of macromolecules will decrease in polypropylene resin, an orientation crystal decreases to the fiber after extension, or yarn, the melting temperature of fiber or yarn becomes low as the result, and it becomes unsuitable as cement reinforcing materials. Furthermore, it is desirable that the molecular weight distributions (Mw/Mn) of gay polypropylene are 3.5-12, and it is desirable that it is especially 4-9.
[0011] In the gay polypropylene resin used by this invention, the well-known modifier for polyolefines can be used together suitably conventionally according to the purpose of use. For example, they are an antioxidant, an ultraviolet ray absorbent, a light stabilizer, crystal ******, an organic carboxylic acid, an antistatic agent, a surfactant, a neutralizer, a dispersant, an epoxy stabilizer, a plasticizer, lubricant, an antimicrobial agent, a flame retarder, a bulking agent, a foaming agent, a foaming assistant, a cross linking agent, a bridge formation assistant, a pigment, etc. As an antioxidant, a phenol system antioxidant, the Lynn system antioxidant, a sulfur system antioxidant, an amine system antioxidant, and vitamins are mentioned. As a neutralizer which served as the dispersant, a metallic soap, hydrotalcites, a lithium aluminum compound hydroxide salt, a silicate, a metallic oxide, a metal hydroxide, etc. are mentioned. Moreover, in order to raise the fiber in the inside of cement, or the dispersibility of yarn, it is also effective to add hydrophilic polymer, such as a polyethylene glycol and a polyethylene oxide, within the limits of 0.1 - 20 weight section.
[0012] 2. A high thermal-resistance polypropylene fiber, the high thermal-resistance polypropylene fiber of the manufacture method this invention of yarn, or yarn extends the above-mentioned gay polypropylene resin after melting fabrication for non-extended fiber, makes it fiber or yarn, further, under restricted strain, heat-treats and is obtained.
[0013] Manufacture of non-extended fiber makes a gay polypropylene resin raw material the shape of the shape of a pellet, and powder, and, generally is performed by the melting extrusion method. For example, non-extended thread is obtained using multifilament melt spinning equipment or monofilament melt spinning equipment. Moreover, after extruding through a flat die or a ring die, the tape for extension (split yarn) is obtained by judging. Subsequently, it extends with extension equipment.
[0014] Extension operation can be performed with multi-stage [one step or two steps or more of]. The range of extension temperature is 70-150 degrees C, and it performs extension operation by making oven, a hot platen, a heating draw roll, far infrared rays, warm water (wet heat), etc. into a heat source. In the case of fiber, in the case of two to 7 times, and yarn, draw magnification is four to 18 times preferably two to 20 times 1.5 to 10 times. When performing extension operation with multi-stage, temperature can be raised gradually and, finally extension operation can also be performed in a 160-195-degree C temperature field. In this case, the below-mentioned heat treatment can also be simplified or omitted. That is, heat treatment under restricted tonus can be performed

with in-line by setting the draw roll temperature in the case of extension as 160-190 degrees C.
[0015] As for an extension polypropylene fiber or yarn, it is desirable that the dissolution peak temperature measured in the state of the restraint is in 180 degrees C or more. That is, the state which restrained the extension polypropylene fiber or yarn before the below-mentioned heat treatment, and after specifically twisting around metals, such as an aluminum board, so that fiber may not contract, it is in the state supplied to the pan for DSC measurement, and when the dissolution peak of the result measured by part for scan speed/of 10 degrees C is in 180 degrees C or more, it can consider as the fiber or the yarn which can be equal to the below-mentioned heat treatment. When the dissolution peak concerned is less than 180 degrees C, since fiber or yarn dissolves at the time of heat treatment under the restricted tonus in an elevated temperature, it is not desirable.
[0016] The above-mentioned polypropylene fiber or above-mentioned yarn extended and obtained heat-treats at 170-195 degrees C under restricted strain. Although it is the range of 130-150 degrees C preferably and 120-160 degrees C of heat treatments were generally performed conventionally By carrying out restricted strain of the extension fiber, and heat-treating at an elevated temperature in this invention Crystallization of the orientation crystal section becomes easy to advance, high-melting point-ization is brought about, extension fiber and yarn do not dissolve in the temperature beyond the original melting point, but the fiber obtained is a low contraction and finds out a bird clapper to a high-melting point.
[0017] namely, the bottom of restricted strain -- the heat treatment temperature of 170-195 degrees C -- desirable -- 175-190 degrees C and heat treatment time 2- the rate of the thermal contraction [rate / for 10 minutes / 170 degrees C of a polypropylene fiber and / of a thermal contraction] for 175 degrees C and 10 minutes can be preferably made 10% or less 10% or less by performing heat treatment for 5 - 40 minutes for 60 minutes Furthermore, the dissolution peak standup temperature in DSC measurement, dissolution peak temperature, and dissolution end temperature can be shifted to an elevated-temperature side, and dissolution peak temperature can be made into 178 degrees C or more. If dissolution peak temperature reaches that heat treatment temperature is less than 170 degrees C only to about 173 degrees C with the fiber of low draw magnification, and yarn but it exceeds 195 degrees C, since fiber or yarn dissolves, heat treatment will become impossible.
[0018] 3. The fiber for cement reinforcement and the high thermal-resistance polypropylene fiber of a strengthening cement moldings this invention, or yarn has a low rate of a thermal contraction under an elevated temperature as mentioned above, and since the melting point has shifted to an elevated-temperature side, it can be used as fiber for cement reinforcement. Even if it performs autoclave curing of 175-180-degree C cement concrete especially, the form is held and fully demonstrates the function as a reinforcement.
[0019] As cement in the case of applying the high thermal-resistance polypropylene fiber or yarn of this invention as cement reinforcing materials, special cement, such as non-hydraulic cement, such as hydraulic cements, such as Portland cement, a white portland cement, alumina cement, a pozzolanic cement, magnesia cement, and Pozzolan cement, plaster, and coal, and an acid resisting cement, etc. can usually be mentioned, for example.
[0020] Moreover, it can obtain by blending thermosetting water soluble resins, such as the aggregates, such as a pebble and sand, pulp, paraffin, a wax, and resol type phenol resin, various kinds of polymer emulsions, a hardening accelerator, a concrete retarder, a water reducing agent, etc. with one sort or two sorts or more in the cement mentioned above as a cement constituent using the above-mentioned cement inorganic material, such as a calcium carbonate, a magnesium hydroxide, or a titanium white, and if needed, for example. When stiffening this cement constituent, as for the mixing ratio of the cement at the time of adding water to a cement constituent, and water, and the so-called C/W ratio, it is desirable to consider as the range of 1-10. The amount of a C/W ratio of water increases too much less than in one, the intensity of a cement hardened material does not become high enough, but if 10 is exceeded, the fluidity of a cement constituent will get worse.
[0021] It faces using the high thermal-resistance polypropylene fiber or yarn of this invention as cement reinforcing materials, and the forms used with the configuration differ. For example, when making yarn into cement reinforcing materials, in the stage which the above-mentioned cement constituent has not hardened completely, yarn is fixed to the semi-hardening object of a cement

constituent by the rock bolt etc., and the method of supplying a cement constituent further etc. is used. Moreover, in using fiber as cement reinforcing materials, after cutting fiber in length of 3-30mm preferably, it is desirable to mix and use into the above-mentioned cement constituent. In this case, since it becomes impossible to acquire sufficient reinforcement effect as it is hard coming to distribute in a cement constituent uniformly and is less than 3mm conversely when fiber length exceeds 30mm, it is not desirable.

[0022] Moreover, the amount in which cement reinforcing materials are made to mix has desirable 0.1 - 30 weight section to the cement constituent 100 weight section, and its 0.5 - 15 weight section is especially desirable. If the amount of cement reinforcing materials cannot acquire reinforcement effect sufficient in under the 0.1 weight section but exceeds 30 weight sections, it will be hard coming to distribute cement reinforcing materials uniformly.

[0023] In addition, in case a polypropylene fiber or yarn is mixed in a cement constituent etc. as cement reinforcing materials, in order to raise compatibility with cement etc., processing with a surfactant etc. is desirable.

[0024] Various cement products are mentioned as a fiber strengthening cement moldings using the high thermal-resistance polypropylene fiber or yarn of this invention. For example, the structures, such as passages, such as the underwater structures, such as a tetrapod, a bridge, and a tunnel, the structure for railroads and a building, a residence (interior material, sheathing material), and a wall surface, a revetment block, a tile, etc. can be mentioned.

[0025]

[Example] Although an example explains this invention below, this invention is not limited only to an example. In addition, the examining method in an example is as follows.

[0026] (1) IPF : it is an isotactic molar fraction in the pentad unit in the polypropylene chain measured by ray ZAMBERI and others (A. Zambelli) using the nuclear-magnetic-resonance spectrum (13 C-NMR) by isotope carbon according to Macromolecules, six volumes, and the method announced by 925 pages (1973). That is, an isotactic pentad molar fraction is a molar fraction of the propylene unit in which five propylene monomeric units carried out isotactic combination continuously. However, about attribution of a peak, it carried out based on Macromolecules, eight volumes, and the revised edition of the above-mentioned reference of a 687 pages (1975) publication. Specifically, the isotactic pentad unit was measured with the on-the-strength molar fraction of the mmmm peak in a full energy peak of the methyl carbon field of 13 C-NMR spectrum.

[0027] (2) It measured at 2.16kg of loads, and 230 degrees C by MFR:JIS K 7210.

(3) It measured in Mw/Mn(molecular weight distribution):GPC.

[0028] (4) Dissolution peak temperature under a restraint : it adjusted so that sample about 4mg of fiber or yarn might be twisted around an aluminum board and fiber might not contract in a temperature up, and dissolution peak temperature was measured in a part for scanning temperature/of 10 degrees C from the room temperature.

[0029] (5) Dissolution peak standup temperature, dissolution peak temperature, and dissolution end temperature : it measured in a part for scanning temperature/of 10 degrees C from the room temperature about sample about 10mg of extension fiber or yarn by DSC (differential scanning calorimetry). However, dissolution peak standup temperature was made into the intersection of the base line and a dissolution peak standup tangent.

[0030] (6) The rate of a thermal contraction : a polypropylene fiber or yarn was held for 10 minutes in oven (170 degrees C and 175 degrees C), and the contracted rate was made into the rate of a thermal contraction.

[0031] (7) Fiber gestalt retentivity after autoclave curing : the concrete test piece was broken after the regimen within the autoclave, and the following criteria estimated from the state configuration of the fiber which remains in the cross section.

O : the thing in the state where the configuration of the thread of a cross section remained completely.

**: What a part of configuration of the thread of a cross section melts, and gestalt change is regarded as.

x: The configuration of the thread of a cross section melts and gestalt change is remarkable.

[0032] Molecular weight distribution 97.2% for 1.5g / 10 minutes to the gay polypropylene powder of 4.5 [example 1IPF] [MFR] Respectively tetrakis [methylene-3-(3, 5-G t-butyl-4-hydroxyphenyl) propionate] methane and a tris (2, 4-G t-buthylphenyl) force fight (all are the Ciba Specialty Chemicals make) as an antioxidant The 0.05 weight section, After blending calcium stearate, using 0.05 weight ****** and a super mixer as a neutralizer, melting kneading was carried out with the screw speed of 230 degrees C and 75rpm with the extruding press machine of 50mmphi, and pellet-like polypropylene was obtained.
[0033] Melt spinning of this was carried out using the multifilament spinning machine with a gear pump (dice : 0.8mm phix30 holes) by part for 300m/in the spinning temperature of 280 degrees C, and winding speed, and about 20-denier non-extended thread was obtained. Subsequently, it extended under conditions with a part for feed speed 50m/, the feed roll temperature of 90 degrees C, 130 degrees C [of heater temperature of an extending point], and a draw roll temperature of 160 degrees C, and extension thread was obtained 3.7 times by the 4.0 times as many highest draw magnification as this. The DSC chart which measured the dissolution peak temperature under the restraint of extension thread is shown in drawing 1 . Dissolution peak temperature was 201 degrees C.
[0034] After fixing ends so that the obtained extension thread may not be contracted with heat, it heat-treated by having put in for 30 minutes into 180-degree C reduction-gear oven, and the heat-resistant polypropylene fiber was obtained. The dissolution peak standup temperature, the dissolution peak temperature, the dissolution end temperature, and the rate of a thermal contraction of the obtained fiber were measured. The result is shown in Table 1. In addition, the DSC chart which measured dissolution peak temperature etc. is shown in drawing 2 .
[0035] in order to raise compatibility with cement to the extension fiber after heat treatment obtained as mentioned above -- a polyoxy-alkylene-glycol system surfactant (tradename: -- LEO contest 1015B --) After applying lion company make (it is 0.1 % of the weight to fiber) and cutting in length of 15mm, an ordinary portland cement (Taiheiyo Cement Corp. make), No. 8 silica sand, pulp, and water by the weight ratio ordinary-portland-cement: -- silica sand: -- pulp: -- it blended and supplied in the becoming cement constituent so that it might be set to water =100:100:3:60, and stirring mixture was carried out using the Omni mixer in addition, the mixing ratio of a cement constituent and the above-mentioned fibrous cement reinforcing materials -- a capacity factor -- cement constituent: -- fibrous -- it was referred to as cement reinforcing materials =100:1
[0036] The cement-fibrous cement reinforcing materials mixture obtained as mentioned above was slushed into the mold with a length of 80mm, a width of face [of 30mm], and a height of 20mm, and, subsequently autoclave curing was performed for the following low pressure steam curing on the 1st on the 1st. The obtained concrete test piece was broken and the fiber form was observed. The result is shown in Table 1.
[0037] Low pressure steam curing: Carry out an isothermal regimen for 3 to 5 hours after recuperating oneself at 23 degrees C for 2 to 5 hours and raising at 20 degrees C/hour in speed to 65 degrees C. It cools slowly to 23 degrees C over 10 - 15 hours after that.
[0038] Autoclave curing: Maintain **, such as an isothermal, for 3 hours after supplying to an autoclave iron pot, applying for 3 hours, after unmolding, and heating and pressurizing to 160 degrees C and ten atmospheric pressure. Heating pressurization is carried out to 180 degrees C and ten atmospheric pressure over 1 hour after that, and next, water is filled in the space of the outer wall of an iron pot, and it cools over 7 - 10 hours to it.
[0039] 170 degrees C and the rate of a thermal contraction for 10 minutes were 0%, the dissolution peak standup temperature of the fibrous cement reinforcing materials by DSC measurement itself, dissolution peak temperature, and dissolution end temperature are 175 degrees C, 179 degrees C, and 184 degrees C, respectively, and marked melting point elevation being seen compared with the former, consequently holding the fiber gestalt after autoclave curing in 180 degrees C was checked as shown in Table 1 and drawing 2 .
[0040] Except having made example 2 heat-treatment temperature into 183 degrees C, like the example 1, fibrous cement reinforcing materials 3.7 times the draw magnification of this were obtained, and the test sample was obtained like the example 1. A result is shown in Table 1 and drawing 2 . Consequently, 170 degrees C and the rate of a thermal contraction for 10 minutes are

0%, and it was checked that 177 degrees C, 182 degrees C, 187 degrees C, and a marked melting point rise are seen, respectively, and the dissolution peak standup temperature by DSC measurement, dissolution peak temperature, and dissolution end temperature hold the fiber form after autoclave curing in 180 degrees C.

[0041] Like the example 1, fibrous cement reinforcing materials 3.2 times the draw magnification of this were obtained, and example 3IPF obtained the test sample like the example 1, except that MFR used 96.8% and molecular weight distribution used the gay polypropylene powder of 4.7 for 0.5g / 10 minutes. A result is shown in Table 1 and drawing 2 . Consequently, 170 degrees C and the rate of a thermal contraction for 10 minutes are 0%, and it was checked that 176 degrees C, 181 degrees C, 185 degrees C, and a marked melting point rise are seen, respectively, and the dissolution peak standup temperature by DSC measurement, dissolution peak temperature, and dissolution end temperature hold the fiber form after autoclave curing in 180 degrees C.

[0042] MFR 97.0% 2g / 10 minutes, [example 4IPF] Molecular weight distribution to the gay polypropylene powder of 4.5 as an antioxidant Respectively tetrakis [methylene-3-(3, 5-G t-butyl-4-hydroxyphenyl) propionate] methane and a tris (2, 4-G t-buthylphenyl) force fight (all are the Ciba Specialty Chemicals make) The 0.05 weight section, As a neutralizer the 0.05 weight section, 2, the 5-dimethyl -2, and 5-di-tert-butyl peroxide hexane (par hexa 25B; Nippon Oil & Fats Co., Ltd. make) for calcium stearate 0.04 weight ******, After blending using a super mixer, melting kneading was carried out with the screw speed of 230 degrees C and 75rpm with the extruding press machine of 50mmphi, MFR obtained and molecular weight distribution obtained the polypropylene of the shape of a pellet of 3.7 for 10g / 10 minutes.

[0043] Melt spinning of this was carried out using the multifilament spinning machine with a gear pump (dice : 0.8mm phix30 holes) by part for 300m/in the spinning temperature of 280 degrees C, and winding speed, and about 20-denier non-extended thread was obtained. Subsequently, it extended under conditions with a part for feed speed 50m/, the feed roll temperature of 90 degrees C, 130 degrees C [of heater temperature of an extending point], and a draw roll temperature of 160 degrees C, and extension thread was obtained 4.5 times. The DSC chart which measured the dissolution peak temperature under the restraint of extension thread is shown in drawing 1. Dissolution peak temperature was 183 degrees C.

[0044] After fixing ends so that the obtained extension thread may not be contracted with heat, it heat-treated by having put in for 30 minutes into 180-degree C reduction-gear oven, and the heat-resistant polypropylene fiber was obtained. The dissolution peak standup temperature, the dissolution peak temperature, the dissolution end temperature, and the rate of a thermal contraction of the obtained fiber were measured. The result is shown in Table 1 and drawing 2 .

[0045] The form after autoclave curing as well as an example 1 was observed using the fibrous cement reinforcing materials of the obtained heat-resistant polypropylene fiber. Consequently, 170 degrees C and the rate of a thermal contraction for 10 minutes are 0%, and it was checked that 174 degrees C, 179.5 degrees C, 185 degrees C, and a marked melting point rise are seen, respectively, and the dissolution peak standup temperature by DSC measurement, dissolution peak temperature, and dissolution end temperature hold the fiber form after autoclave curing in 180 degrees C.

[0046] 110 degrees C of draw roll temperature at the time of example of comparison 1 extension were carried out, except having not heat-treated, like the example 1, fibrous cement reinforcing materials 3.7 times the draw magnification of this were obtained, and various physical-properties values were measured like the example 1, and the form after autoclave curing was observed. The result is shown in Table 1 and drawing 2 . Consequently, 170 degrees C and the rate of a thermal contraction for 10 minutes were 77%, the dissolution peak standup temperature by DSC measurement, dissolution peak temperature, and the dissolution end temperature of 158 degrees C, 165 degrees C, 173 degrees C, and the melting point were low respectively, and it was checked after autoclave curing in 180 degrees C that the fiber form is not held.

[0047] Except having carried out 110 degrees C of draw roll temperature at the time of example of comparison 2 extension, and having made heat treatment temperature into 165 degrees C, like the example 1, fibrous cement reinforcing materials 3.7 times the draw magnification of this were obtained, and various physical-properties values were measured like the example 1, and the form was observed. The result is shown in Table 1 and drawing 2 . Consequently,

170 degrees C and the rate of a thermal contraction for 10 minutes were 65%, the dissolution peak standup temperature by DSC measurement, dissolution peak temperature, and the dissolution end temperature of 167 degrees C, 169 degrees C, 177 degrees C, and the melting point were low respectively, and it was checked after autoclave curing in 180 degrees C that most of the fiber form is not held.

[0048] Except that MFR used 94.2% for 2g / 10 minutes, and molecular weight distribution used [example of comparison 3IPF] the gay polypropylene powder of 5.2, and draw roll temperature was made into 110 degrees C and they made heat treatment temperature 155 degrees C, like the example 1, fibrous cement reinforcing materials 4.0 times the draw magnification of this were obtained, and various physical-properties values were measured like the example 1, and the form after autoclave curing was observed. The result is shown in Table 1. Consequently, could dissolve 170 degrees C and the rate of a thermal contraction for 10 minutes, and they could not be measured, but the dissolution peak standup temperature by DSC measurement, dissolution peak temperature, and the dissolution end temperature of 158 degrees C, 163 degrees C, 168 degrees C, and the melting point were low respectively, and it was checked after autoclave curing in 180 degrees C that the fiber form is not held.

[0049] In the example 3 of example of comparison 4 comparison, when heat treatment temperature was made into 170 degrees C, fiber was not able to fuse during heat treatment and fibrous cement reinforcing materials were not able to be obtained.

[0050] Except that MFR used 96.7% for 40g / 10 minutes, and molecular weight distribution used [example of comparison 5IPF] the gay polypropylene powder of 4.2, and 250 degrees C and draw roll temperature were made into 110 degrees C and they made heat treatment temperature 160 degrees C for spinning temperature, like the example 1, fibrous cement reinforcing materials 5.0 times the draw magnification of this were obtained, and various physical-properties values were measured like the example 1, and the form after autoclave curing was observed. The result is shown in Table 1. Consequently, could dissolve 170 degrees C and the rate of a thermal contraction for 10 minutes, and they could not be measured, but the dissolution peak standup temperature by DSC measurement, dissolution peak temperature, and the dissolution end temperature of 161 degrees C, 166 degrees C, 173 degrees C, and the melting point were low respectively, and it was checked after autoclave curing in 180 degrees C that the fiber form is not held.

[0051] In the example 5 of example of comparison 6 comparison, when heat treatment temperature was made into 170 degrees C, fiber was not able to fuse during heat treatment and fibrous cement reinforcing materials were not able to be obtained.

[0052]

[Table 1]

	ポリプロピレン樹脂			延伸倍率(倍)	延伸糸の拘束下融解ピーク温度(℃)	拘束緊張下の熱処理温度(℃)	耐熱性ポリプロピレン繊維の物性					オートクレーブ養生後の繊維形態保持性
	IPF(%)	MFR(g/10min)	Mw/Mn				融解ピーク立ち上がり温度(℃)	融解ピーク温度(℃)	融解終了温度(℃)	熱収縮率@170℃(%)	熱収縮率@175℃(%)	
実施例1	97.2	1.5	4.5	3.7	201	180	175	179	184	0	7.7	○
実施例2	97.2	1.5	4.5	3.7	201	183	177	182	187	0	6.4	○
実施例3	96.8	0.5	4.7	3.2	202	180	176	181	185	0	7.2	○
実施例4	97	10.0	3.7	4.5	183	180	174	179.5	185	0	9.3	○
比較例1	97.2	1.5	4.5	3.7	201	無	158	165	173	77	融解	×
比較例2	97.2	1.5	4.5	3.7	201	165	167	169	177	65	融解	×
比較例3	94.2	2.0	5.2	4.0	170	155	158	163	168	融解	融解	×
比較例4	94.2	2.0	5.2	4.0	170	170	−	−	−	−	−	−
比較例5	96.7	40.0	4.2	5.0	172	160	161	166	173	融解	融解	×
比較例6	96.7	40.0	4.2	5.0	172	170	−	−	−	−	−	−

[0053]

[Effect of the Invention] since the polypropylene fiber or the yarn of this invention is heat-treating at the elevated temperature under the restricted strain after extension using specific fluid gay polypropylene resin with high stereoregularity -- the rate of a thermal contraction in an elevated temperature -- it is low, and since it is the high high thermal-resistance polypropylene fiber or the yarn of the melting point, even if it uses as fiber for cement reinforcement, the fiber form is maintained under severe care of health, and the effect as a reinforcing agent can fully demonstrate

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[Translation done.]

L6 ANSWER 4 OF 26 CAPLUS COPYRIGHT 2003 ACS on STN
AN 2002:862338 CAPLUS
DN 138:256484
TI Crystal modification in polypropylene fibers containing β-form nucleating agent
AU Takahashi, Tetsuya
CS Faculty of Education, Shimane University, Matsue, Shimane, 690-8504, Japan
SO Sen'i Gakkaishi (2002), 58(10), 357-364
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PB Sen'i Gakkai
DT Journal
LA English
CC 40-4 (Textiles and Fibers)
AB Sample fibers were prepared with a multi-filament melt-spinning machine, from polypropylene (hereafter "PP") to which β-form nucleating agent had been added. The relations between melt-spinning conditions and crystal modification of obtained fibers were studied. Wide-angle x-ray diffraction measurement of fibers yielded the following results: the diffraction peaks of α-form crystal were clearly observed in undrawn fiber to which β-form nucleating agent had been added in an amount of 0.05 wt%. The diffraction peaks of β-form crystal were observed in undrawn fiber to which β-form nucleating agent had been added in an amount of more than 0.10 wt%. Also, the effects of spinning temperature on PP to which β-form nucleating agent had been added in an amount of 0.10 wt% were studied. Only crystalline reflections of α-form were found in the sample produced at a spinning temperature lower than 250°C. However, the reflections of β-form appeared when spinning temperature was increased to 280°C. When the draft ratio was more than 3100, the diffraction peaks of β-form crystal were not observed When the samples were drawn with a heated roller at 110°C, a few diffraction peaks of β-form crystal were found when the draw ratio was set at 4.0, but the peaks were never found when the draw ratio exceeded 5.0. The results indicate that crystal transformation from β-form to α-form takes place in samples for which the crystallite-orientation factor of β-form, fC(β), reaches about 0.788.
ST polypropylene fiber modification crystal nucleating agent
IT Crystal **nucleating agents**
Crystal orientation
(crystal modification in **polypropylene fibers** containing β-form nucleating agent)
IT **Polypropene fibers**, uses
RL: POF (Polymer in formulation); PRP (Properties); USES (Uses)
(crystal modification in **polypropylene fibers** containing β-form nucleating agent)
IT 25085-53-4, Isotactic polypropylene
RL: PEP (Physical, engineering or chemical process); POF (Polymer in formulation); PRP (Properties); PYP (Physical process); PROC (Process); USES (Uses)
(crystal modification in **polypropylene fibers** containing β-form nucleating agent)
RE.CNT 16 THERE ARE 16 CITED REFERENCES AVAILABLE FOR THIS RECORD
RE
(1) Awaya, H; Nippon Kagaku Kaishi 1962, V83, P865 CAPLUS
(2) Chen, X; Int Polym Process 1991, V6, P337 CAPLUS
(3) Chu, F; Polymer 1995, V36, P2523 CAPLUS
(4) Chu, F; Polymer 1996, V37, P573 CAPLUS
(5) Fujiyama, M; J Appl Polym Sci 1988, V36, P985 CAPLUS
(6) Fujiyama, M; J Appl Polym Sci 1988, V36, P995 CAPLUS
(7) Fujiyama, M; J Appl Polym Sci 1991, V42, P2749 CAPLUS
(8) Jones, A; Makromol Chem 1964, V75, P134
(9) Kamide, K; Sen'I Gakkaishi 1969, V25, P53 CAPLUS
(10) Li, J; J Vinyl Addit Technol 1997, V3, P151 CAPLUS
(11) Marcincin, A; J Therm Anal 1996, V46, P581 CAPLUS
(12) Padden, F; J Appl Phys 1959, V30, P1479 CAPLUS
(13) Shi, G; Int Polym Process 1995, V10, P330 CAPLUS
(14) Tjong, S; Polymer 1996, V37, P2309 CAPLUS
(15) Urabe, Y; Reports Progress Polymer Phys 1965, V8, P151
(16) Yang, J; Polymer 1996, V37, P5959 CAPLUS

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POLYPROPYLENE FIBER WITH HIGH HEAT RESISTANCE

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[There are no amendments to this patent.]

Abstract

Purpose

The purpose of the present invention is to produce a polypropylene fiber or yarn with high heat resistance suitable for use as a cement reinforcement material that does not undergo fusion at autoclave curing temperatures in the range of 175-180°C and that has superior shape retention.

Means to solve

In a polypropylene fiber or yarn with high heat resistance produced by hot-melt molding a homopolypropylene resin having an isotactic pentad fraction in the range of 96-98.5% and melt-flow rate (230°C, 2.16 kg load) in the range of 0.1-30 g/10 min and drawing, a polypropylene fiber or yarn with high heat resistance characterized by the fact that the heat shrinkage factor at 170°C for 10 min is 10% or below and the fusion peak temperature is 178°C or above.

Claim

1. A polypropylene fiber or yarn with high heat resistance produced by hot-melt molding a homopolypropylene resin having an isotactic pentad fraction in the range of 96-98.5% and melt-flow rate (230°C, 2.16 kg load) in the range of 0.1-30 g/10 min and drawing, which polypropylene fiber or yarn with high heat resistance is characterized by the fact that the heat shrinkage factor at 170°C for 10 min is 10% or below and the fusion peak temperature is 178°C or above.

2. The polypropylene fiber or yarn with high heat resistance described in Claim 1, characterized by the fact that a heat treatment is provided for the polypropylene fiber or yarn

with high heat resistance after drawing at a temperature in the range of 170-195°C under restraint tension.

3. The polypropylene fiber or yarn with high heat resistance described in Claim 1 or 2, characterized by the fact that the fusion peak of the polypropylene fiber or yarn with high heat resistance before the heat treatment with restraint measured under restraint tension exists at 180°C or above.

4. A cement reinforcement fiber made of the polypropylene fiber or yarn with high heat resistance described in one of Claims 1-3.

Detailed explanation of the invention

[0001]

Technical field of the invention

The present invention pertains to a polypropylene fiber or yarn with high heat resistance and the invention further pertains to a polypropylene fiber or yarn with high heat resistance used for cement reinforcement fiber.

[0002]

Prior art

Historically, cement moldings are used for building materials such as interiors, exteriors, and roofing. In the past, products containing asbestos fibers have been widely used as reinforcement materials for cement moldings, but with recent environmental problems, the adverse effect of asbestos on health is gaining attention and use of replacement fibers is increasing each year. For reinforcement fibers to replace the above-mentioned asbestos, polyolefin fibers, in particular, polypropylene fibers and polyethylene fibers can be mentioned, and their use is on the increase as replacement fibers that can be used without adverse effects on the human body.

[0003]

Cement requires a curing process during molding. Curing is achieved in an autoclave (10 kgf/cm^2) for several tens of hours at a temperature in the range of 170-180°C. However, the fusion point of standard polypropylene fibers is in the range of 160-165°C; thus, fusion takes place during the aforementioned curing and the polypropylene fails to exist in the cement concrete after curing. When the curing temperature for the cement concrete is reduced to 165-170°C, for example, a long curing time is required and productivity is reduced.

[0004]

Problems to be solved by the invention

Based on the above background, the purpose of the present invention is to produce a polypropylene fiber or yarn with high heat resistance suitable for use as a cement reinforcement material that does not undergo fusion in an autoclave at a curing temperature of 175-180°C and that has superior shape retention.

[0005]

Means to solve the problems

As a result of much research conducted by the present inventors in an effort to eliminate the above-mentioned existing problems, the researchers discovered that it was possible to control the thermal shrinkage factor under high temperature to a low value and to increase the fusion peak temperature when a heat treatment is provided for a homopolypropylene resin having specific stereoregularity and flow properties at a specific temperature under restraint tension after hot-melt drawing, and as a result, the present invention was accomplished.

[0006]

In other words, the first invention of the present invention is a polypropylene fiber or yarn with high heat resistance characterized by the fact that the heat shrinkage factor at 170°C for 10 min is 10% or below and the fusion peak temperature is 178°C or above in a polypropylene fiber or yarn with high heat resistance produced by hot-melt molding a homopolypropylene resin having an isotactic pentad fraction in the range of 96-98.5% and melt-flow rate (230°C, 2.16 kg load) in the range of 0.1-30 g/10 min and drawing.

[0007]

Furthermore, the second invention of the present invention is the polypropylene fiber or yarn with high heat resistance described in the first invention characterized by the fact that a heat-treatment is provided for the polypropylene fiber or yarn with high heat resistance after drawing at a temperature in the range of 170-195°C under restraint tension.

[0008]

Furthermore, the third invention of the present invention is the polypropylene fiber or yarn with high heat resistance described in the first or second invention characterized by the fact that the fusion peak of the polypropylene fiber or yarn with high heat resistance before the heat-treatment with restraint measured under restraint tension exists at 180°C or above.

[0009]

Furthermore, the fourth invention of the present invention is a cement reinforcement fiber made of the polypropylene fiber or yarn with high heat resistance described in the first to the third inventions.

[0010]

Embodiment of the invention

In the following, the present invention is explained in further detail.

1. Polypropylene resin

The polypropylene resin used in the present invention is a homopolypropylene resin having an isotactic pentad fraction (hereinafter referred to as IPF), which is the index of stereoregularity, of 96-98.5% and satisfies the melt-flow rate (hereinafter referred to as MFR) of 0.1-30 g/10 min, preferably, 0.5-25 g/10 min at 230°C and under a load of 2.16 kg. When the IPF is 96% or below, the fusion temperature of the homopolypropylene itself is reduced, and it is not suitable to be used as a cement reinforcement material; on the other hand, when the IPF is 98.5% or above, spinning stability such as stability of the thread is lost as a result of an excessively high rate of crystallization of the molten resin at the time of hot-melt spinning. Furthermore, when the MFR is 0.1 g/10 min or below, an increase in the pressure at the die exit occurs at the time of hot-melt molding (mainly at the time of spinning of the fiber); on the other hand, when the MFR is 30 g/10 min or above, the polymer component is reduced in the polypropylene resin, oriented crystals in the fiber or yarn are reduced after drawing, and as a result, the fusion temperature of the fiber or yarn is reduced, and the material is not suitable to be used as a cement reinforcement material. It is further desirable when the molecular weight distribution (Mw/Mn) of the homopolypropylene is in the range of 3.5-12, and 4-9 is further desirable.

[0011]

For the homopolypropylene resin used in the present invention, conventional modifiers for polyolefins may be used in combination according to the intended application. For example, antioxidants, ultraviolet absorbers, light stabilizers, crystalline nucleating agents, organic carboxylic acids, antistatic agents, surfactants, neutralizing agents, dispersants, epoxy stabilizers, plasticizers, lubricants, antibacterial agents, flame retardants, fillers, blowing agents, foaming co-agents, crosslinking agents, crosslinking co-agents, pigments, etc., can be mentioned. For antioxidants, phenolic antioxidants, phosphoric antioxidants, sulfur type antioxidants, amine type antioxidants, vitamins, etc., can be mentioned. For neutralizing agents that double as dispersants,

metal soaps, hydrotalcites, lithium aluminum composite hydroxylate, silicates, metal oxides, metal hydroxides, etc., can be mentioned. Furthermore, it is effective to add 0.1-20 parts by weight of a hydrophilic polymer such as polyethylene glycol and polyethylene oxide so as to increase dispersibility of the fiber or yarn in the cement.

[0012]

2. Method for production of polypropylene fiber or yarn with high heat resistance

The polypropylene fiber or yarn with high heat resistance of the present invention is produced by hot-melt molding the above-mentioned homopolypropylene resin to form an amorphous fiber, drawing to form a fiber or yarn, and providing a heat treatment under restraint tension.

[0013]

In general, an amorphous fiber is produced by the hot-melt molding method using a pellet type or powder type homopolypropylene resin raw material. For example, a multifilament hot-melt spinning device or monofilament hot-melt spinning device is used to produce an amorphous yarn. Furthermore, when the material is cut after passing through the flat die or ring die, a tape for drawing (split yarn) is produced. Subsequently, drawing is done with a drawing machine.

[0014]

Drawing is achieved in a single stage or in a multistage device consisting of two or more stages. The drawing temperature is in the range of 70-150°C and the drawing operation is done using an oven, a hot plate, hot drawing roll, infrared, hot water (wet heat), etc., as a heat source. The drawing ratio is in the range of 1.5-10 times, preferably, 2-7 times, for fibers, and 2-20 times, preferably, 4-18 times, for a yarn. When drawing is done in a multistage device, the temperature can be increased in a stepwise fashion and final drawing is done at a temperature in the range of 160-195°C. In this case, the heat treatment described below may be omitted. In other words, when the drawing roll temperature at the time of drawing is set to a temperature in the range of 160-190°C, an inline heat treatment under restraint tension is made possible.

[0015]

It is desirable when the drawn polypropylene fiber or yarn has a fusion peak temperature measured under a restraint state of 180°C or above. In other words, when the fusion peak measured under restraint tension of the drawn polypropylene fiber or yarn before the heat-treatment described below, in specific terms, when the fusion peak measured at a scanning

rate of 10°C/min as the fiber is wound around a metal such as an aluminum sheet to prevent shrinkage of the fiber and placed on a DSC measurement plate, is 180°C or above, production of a fiber or yarn having an adequate resistance to the heat treatment described below is possible. When the aforementioned fusion peak is 180°C or below, fusion of the fiber or yarn occurs at the time of heat treatment under high temperature and under restraint tension, which is not desirable.

[0016]

A heat treatment is provided for the polypropylene fiber or yarn with high heat resistance drawn as described above under restraint tension at a temperature of 170-195°C. In general, a heat-treatment is provided at a temperature in the range of 120-160°C, preferably in the range of 130-150°C in the past, but crystallization at the oriented crystal part is likely to be promoted when a heat treatment is provided for the drawn fiber under restraint tension in the present invention, and an increase in the fusion point is made possible, and fusion of the drawn fiber or yarn does not occur at a temperature above the fusion point, and production of a fiber with a low shrinkage factor and high fusion point is made possible.

[0017]

In other words, when a heat treatment is applied at a heat-treatment temperature in the range of 170-195°C, preferably 175-190°C, for 2-60 min, preferably 5-40 min, it is possible to achieve a heat shrinkage factor of the polypropylene fiber of 10% or below at 170°C for 10 min, preferably 10% or below at 175°C for 10 min. Furthermore, it is possible to shift the fusion peak start-up temperature, fusion peak temperature, and fusion end temperature at DSC measurement toward the high temperature side, and it is possible to achieve a fusion peak temperature of 178°C or above. When the heat-treatment temperature is 170°C or below, the fusion peak temperature of the fiber or yarn with a low drawing ratio is capable of achieving approximately 173°C, at most, and when the temperature exceeds 195°C, fusion of fiber or yarn takes place and heat treatment is difficult.

[0018]

3. Cement reinforcement fiber and reinforced cement molding

As described above, the heat shrinkage factor is low in the polypropylene fiber or yarn with high heat resistance of the present invention under high temperature and the fusion point is shifted toward the high-temperature side and is suitable to be used as a cement reinforcement fiber. Especially when curing is done in an autoclave used for concrete at a temperature of 175-180°C, the shape is retained and it can be used as effectively as a reinforcement material.

[0019]

For the cement for which the polypropylene fiber or yarn with high heat resistance of the present invention is used as a cement reinforcement material, for example, hydraulic setting cements such as portland cement, white portland cement, aluminous cement, silica cement, magnesia cement, and pozzuolana cement, air-hardening cements such as gypsum and coal, special cements such as acid-resistant cement, etc., can be mentioned.

[0020]

Furthermore, production of a cement composition that utilizes the above-mentioned cement is made possible when an inorganic material such as calcium carbonate and magnesium hydroxide, optional aggregates such as pebbles and sand, thermosetting water-soluble resins such as pulp, paraffin, wax and resol type phenolic resin, a variety of polymer emulsions, curing accelerators, curing inhibitors, water reducing agents, etc., are added to one or more types of the above-mentioned cements. Upon curing of the above-mentioned cement composition, the mixing ratio of the cement and water, when water is added to the cement composition, that is, the C/W ratio, is preferably in the range of 1-10. When the C/W ratio is below 1, the amount of water becomes too high and an adequate strength cannot be achieved upon curing of the cement; on the other hand, when said ratio exceeds 10, the flow properties of the cement composition become inferior.

[0021]

When the polypropylene fiber or yarn with high heat resistance of the present invention is used as a cement reinforcement material, the application form varies depending on the shape of the fiber or yarn. For example, when a yarn is used as the cement reinforcement material, a method where the yarn is fastened to the partially cured cement composition using a lock bolt, etc., and the cement composition is supplied is used. Furthermore, when the fiber is used as a cement reinforcement material, preferably, the fiber is cut to a length of 3-30 mm and mixed in the above-mentioned cement composition. In this case, uniform dispersing of the fiber in the cement composition is less likely to occur when the length of the fiber exceeds 30 mm; on the other hand, an adequate reinforcement effect cannot be achieved at 3 mm or below.

[0022]

Furthermore, in general, the amount of cement reinforcement material used is in the range of 0.1-30 parts by weight for 100 parts by weight of the cement composition, and in the range of 0.5-15 parts by weight is further desirable. When the amount of the cement reinforcement material included is 0.1 part by weight or below, an adequate reinforcement effect

cannot be achieved; on the other hand, when the amount exceeds 30 parts by weight, uniform dispersing of the cement reinforcement material is less likely to be achieved.

[0023]

Furthermore, upon mixing of the polypropylene fiber or yarn with high heat resistance with the cement composition as a cement reinforcement material, it is desirable when a treatment is provided with a surfactant, etc., to increase the affinity with the cement.

[0024]

A variety of cement products can be mentioned as fiber-reinforced cement moldings that utilize the polypropylene fiber or yarn with high heat resistance of the present invention. For example, underwater structures such as tetrapods, railway structures such as bridges and tunnels, structures such as buildings, houses (interiors and exteriors), wall surfaces, revetments, roof tiles, etc., can be mentioned.

[0025]

Application examples

The present invention is explained in further detail below, but the present invention is not limited to the application examples below. Furthermore, test methods used in the present invention are as shown below.

[0026]

(1) IPF

The isotactic factor by pentad unit in the polypropylene molecular chain is measured by a nuclear magnetic resonance spectral analysis (^{13}C-NMR) based on isotopic carbon according to the method reported in Macromolecules, Vol. 6, p. 925 (1973) by A. Zambelli et al. In other words, the isotactic pentad factor is the propylene unit factor where five continuous propylene monomer units are isotactically bonded. Wherein, assignment of the peak is done according to the corrected version of the aforementioned document described in Macromolecules, Vol. 8, p. 687 (1975). In specific terms, measurement of the isotactic pentad unit is done based on the intensity factor of the mmmm peak in the total absorption peak in the methyl carbon region of the ^{13}C-NMR spectra.

[0027]

(2) MFR

According to the specification of JIS K 7210, measurement was done under a load of 2.16 kg and at 230°C.

(3) Mw/Mn (molecular weight distribution)

GPC was used for the measurement.

[0028]

(4) Fusion peak temperature under a restraint state

Approximately 4 mg of a sample fiber or yarn were wrapped around an aluminum sheet and an arrangement was made to prevent shrinkage of the fiber at the time of temperature increase, and the fusion peak temperature was measured at a scanning rate of 10°C/min starting from room temperature.

[0029]

(5) Fusion peak start-up temperature, fusion peak temperature, and fusion end temperature

Approximately 10 mg of drawn sample fiber or yarn were used and the measurement was made by DSC (Differential Scanning Calorimetry) at a scanning rate of 10°C/min starting from room temperature. In this case, the fusion peak start-up temperature is the nodal point of contact of the base line and fusion peak start-up line.

[0030]

(6) Heat shrinkage factor

The polypropylene fiber or yarn with high heat resistance was retained in an oven heated to 170°C and 175°C for 10 min and the shrinkage ratio is defined as the heat shrinkage factor.

[0031]

(7) Fiber shape retention after curing in an autoclave

After curing in an autoclave, the concrete test piece was cracked and an evaluation was made based on the shape of the fiber cross section based on the criteria shown below.

O : complete shape of the fiber is left behind in the cross section.

Δ: fiber is partially dissolved at the cross section and a change of shape is observed.

X: fiber is dissolved and a change of shape is observed in the cross section.

[0032]

Application Example 1

For the homopolypropylene powder with an IPF of 97.2%, MFR of 1.5 g/10 min and molecular weight distribution of 4.5, 0.05 part by weight each of tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate)]methane and tris(2,4-di-t-butylphenyl)phosphite (both products of Chiba Special Chemicals Co.) were added as antioxidants, then, 0.05 part by weight calcium stearate was added as a neutralizing agent, and blending was done in a supermixer, and hot-melt mixing was done by an extruder with a diameter of 50 mmϕ at a temperature of 230°C and screw rotation of 75 rpm to produce polypropylene pellets.

[0033]

Hot-melt spinning was done for the aforementioned pellets by a multifilament spinner (die: 0.8 mmϕ x 30 holes) equipped with a gear pump at a spinning temperature of 280°C and take-up speed of 300 m/min to produce an amorphous yarn of approximately 20 denier. Furthermore, drawing was done at a feed rate of 50 m/min, feed roll temperature of 90°C, heater temperature at a drawing point of 130°C and drawing roll temperature of 160°C to produce a yarn drawn by 3.7 times at a maximum drawing ratio of 4.0 times. The DSC chart obtained by measuring the fusion peak temperature under a restraint state of the drawn yarn is shown in Figure 1. The fusion peak temperature was 201°C.

[0034]

Both ends of the drawn yarn were fastened to prevent shrinkage by heat and it was placed in a gear oven heated to 180°C for 30 min and a heat treatment was applied to produce a heat-resistant polypropylene fiber. Measurements were made of the fusion peak start-up temperature, fusion peak temperature, fusion end temperature, and heat shrinkage factor of the fiber produced. The results obtained are shown in Table 1 below. Furthermore, the DSC chart obtained upon measurement of fusion peak temperature, etc., is shown in Figure 2.

[0035]

In order to increase affinity with the cement, a polyoxyalkylene glycol type surfactant (trade name: Leocon [transliteration] 1015B, product of Lion Co.) was coated onto the drawn fiber produced as described above after the heat treatment (0.1 wt% for the fiber); then, the fiber was cut to form lengths of 15 mm, and added to a cement composition comprising a normal portland cement (product of Taiheiyo Cement Co.), No. 8 quartz sand, pulp, and water at a weight ratio of normal portland cement : No. 8 quartz sand : pulp : water = 100:100:3:60, and stirring and mixing were provided by an Omni mixer. In this case, the mixing ratio of the cement

composition and the above-mentioned fiber-like cement reinforcement material was cement composition:fiber-like cement reinforcement material = 100:1 at a volume ratio.

[0036]

The cement and fiber-like cement reinforcement material mixture produced as described above was poured into a mold form with a length of 80 mm, width of 30 mm, and height of 20 mm and then atmospheric pressure steam curing was provided for one day, and curing in an autoclave was provided for one day. The concrete test piece was cracked and the shape of the fiber was examined. The results obtained are shown in Table 1 below.

[0037]

Atmospheric pressure steam curing: Curing was done for 2-5 h at 23°C and the temperature was increased to 65°C at a rate of 20°C/h, and isothermal curing was done for 3-5 h. Subsequently, the temperature was reduced to 23°C in 10-15 h and slow cooling was achieved.

[0038]

Curing in an autoclave: The mold was removed and the test piece was placed in an autoclave pot, and heated to 160°C and pressurized to 10 atm in 3 h and the isothermal temperature and pressure were retained for 3 h. Subsequently, the temperature was increased to 180°C in 1 h and 10 atm was retained; then, water was poured into the space between the pot and the outer wall and cooling was done over 7-10 h.

[0039]

As shown in Table 1 and Figure 2, the heat shrinkage factor at 170°C for 10 min is 0% and the fusion peak start-up temperature, fusion peak temperature, and fusion end temperature of the fiber-like cement reinforcement material based on DSC measurement were 175°C, 179°C, and 184°C, respectively, and in comparison to the prior art, a significant increase in the fusion point is observed, and furthermore, good shape retention after autoclave curing at 180°C was confirmed.

[0040]

Application Example 2

The heat-treatment temperature was changed to 183°C and production of a fiber-like cement reinforcement material with a drawing ratio of 3.7 times was achieved and a test sample was produced as in Application Example 1. The results obtained are shown in Table 1 and Figure

2. As a result, the heat shrinkage factor at 170°C for 10 min is 0% and the fusion peak start-up temperature, fusion peak temperature, and fusion end temperature of the fiber-like cement reinforcement material based on DSC measurement were 177°C, 182°C, and 187°C, respectively, and a significant increase in the fusion point is observed, and furthermore, good shape retention after autoclave curing at 180°C was confirmed.

[0041]

Application Example 3

A homopolypropylene powder with an IPF of 96.8%, MFR of 0.5 g/10 min, molecular weight distribution of 4.7 was used and production of a fiber-like cement reinforcement material having a drawing ratio of 3.2 was achieved and a test sample was produced as in Application Example 1. The results obtained are shown in Table 1 and Figure 2. As a result, the heat shrinkage factor at 170°C for 10 min is 0% and the fusion peak start-up temperature, fusion peak temperature, and fusion end temperature of the fiber-like cement reinforcement material based on DSC measurement were 176°C, 181°C, and 185°C, respectively, and a significant increase in the fusion point is observed, and furthermore, good shape retention after autoclave curing at 180°C was confirmed.

[0042]

Application Example 4

For a homopolypropylene powder with an IPF of 97.0%, MFR of 2 g/10 min and molecular weight distribution of 4.5, 0.05 part by weight each of tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate)]methane and tris(2,4-di-t-butylphenyl)phosphite (both products of Chiba Special Chemicals Co.) was added as antioxidants; then, 0.05 part by weight calcium stearate was added as a neutralizing agent, and then, 0.04 part by weight of 2,5-dimethyl-2,5-di(t-butylperoxy)hexane (Perhexa [transliteration] 25B, product of Japan Fats and Oils Co.) was added and blending was done by a supermixer, and hot-melt mixing was done by an extruder with a diameter of 50 mmϕ at a temperature of 230°C and screw rotation of 75 rpm to produce a polypropylene pellet with an MFR of 10 g/10 min and molecular weight distribution of 3.7.

[0043]

Hot-melt spinning was conducted for the pellets produced by a multifilament spinner (die: 0.8 mmϕ x 30 holes) equipped with a gear pump at a spinning temperature of 280°C and take-up speed of 300 m/min to produce an amorphous yarn of approximately 20 denier. Furthermore, drawing was done at a feed rate of 50 m/min, feed roll temperature of 90°C, heater

temperature at the drawing point of 130°C and drawing roll temperature of 160°C to produce a yarn drawn to 4.5 times. The DSC chart obtained by measuring the fusion peak temperature under the restraint state of the drawn yarn is shown in Figure 1. The fusion peak temperature was 183°C.

[0044]

Both ends of the drawn yarn were fastened to prevent shrinkage by heat and placed in a gear oven heated to 180°C for 30 min and heat treatment was applied to produce a heat-resistant polypropylene fiber. Measurements were made for the fusion peak start-up temperature, fusion peak temperature, fusion end temperature, and heat shrinkage factor of the fiber produced. The results obtained are shown in Table 1 and Figure 2.

[0045]

The heat-resistant polypropylene fiber cement reinforcement material was used and the state after curing in an autoclave as in the case of Application Example 1 was examined. As a result, the heat shrinkage factor at 170°C for 10 min is 0% and the fusion peak start-up temperature, fusion peak temperature, and fusion end temperature of the fiber-like cement reinforcement material based on DSC measurement were 174°C, 179.5°C, and 185°C, respectively, and a significant increase in the fusion point is observed, and furthermore, good shape retention after autoclave curing at 180°C was confirmed.

[0046]

Comparative Example 1

The drawing roll temperature at the time of drawing was changed to 110°C and the heat treatment was omitted and production of a fiber-like cement reinforcement material with a drawing ratio of 3.7 times was achieved as in Application Example 1, and measurement of each property was done as in Application Example 1 and the state after curing in an autoclave was examined as described above. The results obtained are shown in Table 1 and Figure 2. As a result, the heat shrinkage factor at 170°C for 10 min was 77% and the fusion peak start-up temperature, fusion peak temperature, and fusion end temperature of the fiber-like cement reinforcement material based on DSC measurement were low values of 158°C, 165°C and 173°C, respectively, and good shape retention after autoclave curing at 180°C was absent.

[0047]

Comparative Example 2

The drawing roll temperature at the time of drawing was changed to 110°C and the heat-treatment temperature was changed to 165°C and a fiber-like cement reinforcement material with a drawing ratio of 3.7 times was produced as in Application Example 1, and measurement of each property was done as in Application Example 1 and the state after curing in an autoclave was examined as described above. The results obtained are shown in Table 1 and Figure 2. As a result, the heat shrinkage factor at 170°C for 10 min was 65% and the fusion peak start-up temperature, fusion peak temperature, and fusion end temperature of the fiber-like cement reinforcement material based on DSC measurement were low values of 167°C, 169°C and 177°C, respectively, and good shape retention after autoclave curing at 180°C was absent.

[0048]

Comparative Example 3

A homopolypropylene powder with an IPF of 94.2%, MFR of 2 g/10 min and molecular weight distribution of 5.2 was used and the drawing roll temperature was changed to 110°C and the heat-treatment temperature was changed to 155°C and a fiber-like cement reinforcement material with a drawing ratio of 4.0 was produced as in Application Example 1, and measurement of each property was done as in Application Example 1 and the state after curing in an autoclave was examined as described above. The results obtained are shown in Table 1. As a result, measurement of the heat shrinkage factor at 170°C for 10 min was not possible due to fusion, and the fusion peak start-up temperature, fusion peak temperature, and fusion end temperature of the fiber-like cement reinforcement material based on DSC measurement were low values of 158°C, 163°C and 168°C, respectively, and good shape retention after autoclave curing at 180°C was absent.

[0049]

Comparative Example 4

In Comparative Example 3, when the heat-treatment temperature of 170°C was used, fusion of the fiber took place during the course of the heat treatment and production of a fiber-like cement reinforcement material was not possible.

[0050]

Comparative Example 5

A homopolypropylene powder with an IPF of 96.7%, MFR of 40 g/10 min and molecular weight distribution of 4.2 was used and spinning temperature of 250°C, drawing roll temperature

of 110°C, and heat-treatment temperature of 160°C were used and a fiber-like cement reinforcement material with a drawing ratio of 5.0 times was produced as in Application Example 1, and measurement of each property was done as in Application Example 1 and the state after curing in an autoclave was examined as described above. The results obtained are shown in Table 1. As a result, measurement of the heat shrinkage factor at 170°C for 10 min was not possible due to fusion, and fusion peak start-up temperature, fusion peak temperature, and fusion end temperature of the fiber-like cement reinforcement material based on DSC measurement were low values of 161°C, 166°C, 173°C and 180°C, respectively, and good shape retention after autoclave curing at 180°C was absent.

[0051]

Comparative Example 6

In Comparative Example 5, when the heat-treatment temperature of 170°C was used, fusion of the fiber took place during the course of the heat treatment and production of a fiber-like cement reinforcement material was not possible.

[0052]

Table 1

	ポリプロピレン樹脂			延伸倍率(倍)	延伸糸の拘束下融解ピーク温度(℃)	拘束緊張下の熱処理温度(℃)	耐熱性ポリプロピレン繊維の物性					オートクレーブ養生後の繊維形態保持性
	IPF(%)	MFR(g/10min)	Mw/Mn				融解ピーク立ち上がり温度(℃)	融解ピーク温度(℃)	融解終了温度(℃)	熱収縮率@170℃(%)	熱収縮率@175℃(%)	
実施例1	97.2	1.5	4.5	3.7	201	180	175	179	184	0	7.7	○
実施例2	97.2	1.5	4.5	3.7	201	183	177	182	187	0	6.4	○
実施例3	96.8	0.5	4.7	3.2	202	180	170	181	185	0	7.2	○
実施例4	97	10.0	3.7	4.5	183	180	174	179.5	185	0	9.3	○
比較例1	97.2	1.5	4.5	3.7	201	緩	158	165	173	77	融解	×
比較例2	97.2	1.5	4.5	3.7	201	165	167	169	177	65	融解	×
比較例3	94.2	2.0	5.2	4.0	170	155	158	163	168	融解	融解	×
比較例4	94.2	2.0	5.2	4.0	170	170	−	−	−	−	−	−
比較例5	96.7	40.0	4.2	5.0	172	160	161	166	173	融解	融解	×
比較例6	96.7	40.0	4.2	5.0	172	170	−	−	−	−	−	−

Key: 1 Homopolypropylene resin
2 Drawing ratio (times)
3 Fusion peak temperature of drawn yarn under restraint state (°C)
4 Heat-treatment temperature under restraint tension (°C)
5 Properties of heat-resisting polypropylene fiber
6 Shape retention of fiber after curing in autoclave

7 Fusion peak start-up temperature (°C)
8 Fusion peak temperature (°C)
9 Fusion end temperature (°C)
10 Heat shrinkage factor @ _ (%)
11 Application Example __
12 Comparative Example __
13 None
14 Fusion

[0053]

Effect of the invention

In the polypropylene fiber or yarn with high heat resistance of the present invention, a homopolypropylene resin with high stereoregularity and specific flow properties is used and a heat treatment is provided at a high temperature after drawing under restraint tension; thus, the heat shrinkage factor at high temperature is low and a polypropylene fiber or yarn with high heat resistance with high melting point is produced, and when used as a cement reinforcement fiber, good shape retention can be achieved even under harsh curing conditions, and it can be used effectively as a reinforcement material.

Brief description of the figures

Figure 1 is the DSC measurement chart of the drawn yarns produced in Application examples 1, 2 and 4 under a restraint state.

Figure 2 is the DSC measurement chart of fibers produced in the application examples and comparative examples after heat treatment.

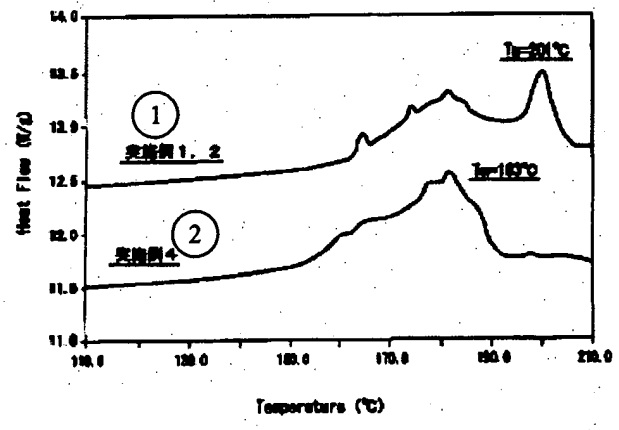

Figure 1

Key: 1 Application Examples 1 and 2
2 Application Example 4

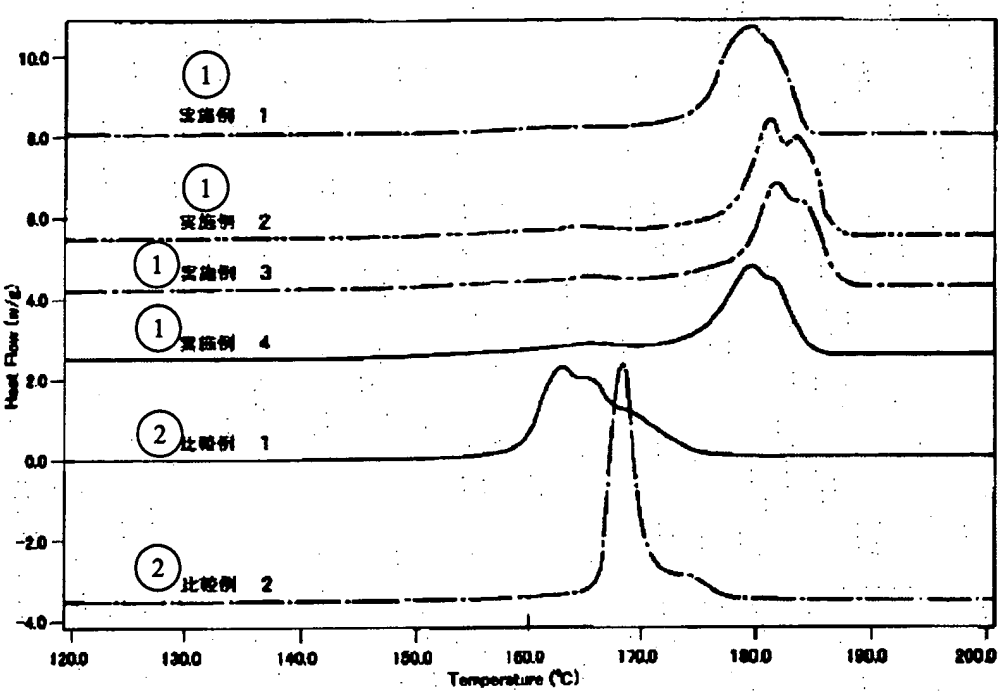

Figure 2

Key: 1 Application Example __
2 Comparative Example __